

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08G 61/00, 61/02, 61/12 C08L 65/00, 65/04	A1	(11) International Publication Number: WO 91/15534 (43) International Publication Date: 17 October 1991 (17.10.91)
(21) International Application Number: PCT/US91/02096 (22) International Filing Date: 27 March 1991 (27.03.91) (30) Priority data: 502,483 30 March 1990 (30.03.90) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (72) Inventors: HAN, Chien-Chung ; 164 Shunpike Road, Madison, NJ 07940 (US). ELSENBAUMER, Ronald, L. ; 24 Black Watch Trail, Morris Township, NJ 07940 (US).	(74) Agent: ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>	
(54) Title: ELECTRICALLY CONDUCTIVE POLY(AROMATIC VINYLENES) AND POLY(HETEROAROMATIC VINYLENES) (57) Abstract <p>This invention relates to novel forms of electrically conductive poly(heteroaromatic vinylenes), and poly(aromatic vinylenes) and to solutions thereof and to processes and precursors for preparing same.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LJ	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LJ	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

ELECTRICALLY CONDUCTIVE POLY(AROMATIC
VINYLENES) AND POLY(HETEROAROMATIC VINYLENES)

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

This invention relates to novel electrically
conductive forms of poly(heteroaromatic vinylenes) and
poly(aromatic vinylenes), to precursors for use in
processes for formation of said poly(aromatic vinylenes)
10 and poly(heteroaromatic vinylenes), and to solutions and
blends comprising poly(aromatic vinylenes) or
poly(heteroaromatic vinylenes) in the conductive form.
Another aspect of this invention relates to methods of
using the solutions and blends of this invention to form
15 conducting polymer articles, including films, fibers, and
coatings and methods of using such solutions as conducting
liquids. Yet another aspect of this invention relates to
novel process for preparing the poly(heteroaromatic
vinylenes) and the poly(aromatic vinylenes) of this
20 invention.

2. Prior Art

There has recently been an increased interest in the
electrical conductivity of polymeric systems. For
25 example, US Patent Nos. 4,321,114 and 4,442,187 are
directed to conjugated polymers having conjugation in all
or a part of at least one backbone chain thereof, such as
polyacetylene, polyphenylene and poly(phenylene sulfide).
It has recently been discovered that these conjugated
30 backbone polymers can be chemically doped in a controlled
manner with electron acceptor and/or electron donor
dopants to produce electrically conducting polymers.
Doping procedures and certain representative doped
polymers are described in US Patent Nos. 4,222,903 and
35 4,204,216.

In the general field of conducting polymers, it is
believed very difficult to dope one of these conjugated

backbone polymers to the extent that it becomes a good conductor (10^{-4} - $100 \text{ ohm}^{-1}\text{cm}^{-1}$) and thereafter dissolve the polymer in any solvent-system. US Patent 4,452,727 and 4,599,194 disclose novel polymer solutions containing a doped sulfur-containing or oxygen-containing aromatic polymer. The solvent of this solution is restricted to solvents containing Lewis Acid halides having a liquid phase under atmospheric pressure for at least one temperature between -150°C and $+100^{\circ}\text{C}$, such as arsenic trifluoride, phosphorus trifluoride, phosphorous pentafluoride, phosphorus trichloride, boron trifluoride and the like. These solutions can be used to form articles, as for example, by casting the solution onto a substrate, and removing the solvent. This solution and method represents a significant advancement over the art; however, it does suffer from certain economic and practical disadvantages resulting from the cost and high environmental reactivity and toxicity of the specific solvents which must be used.

A few conductive species of polyalkylthiophenes are known, having been primarily prepared by electrochemical polymerization. Illustrative of such species are poly(3-methylthiophene) and poly(3,4-dimethylthiophene). R.J. Waltman, J. Bargon and A.F. Diaz, J. Phys. Chem., **87**, 1459-1463, 1983. G. Tourillon, D. Govrier, P. Garnier and D. Viven, J. Phys. Chem., **88**, 1049-1051, 1984. S. Hotta, T. Hosaka and W. Shimotsuma, Syn. Metals., **6**, 317-318, 1983. However, the polymers prepared electrochemically are not soluble in common organic solvents such as acetonitrile,, propylene carbonate, tetrahydrofuran, dichloromethane, dimethyl formamide, nitrobenzene, nitropropane, toluene, and the like. In the absence of solutions, or plasticized forms, the ability to economically fabricate articles out of the conducting forms of these poly(alkylthiophenes), especially semi-conducting and conducting polymer films, fibers, and coatings, especially using conventional solvents or melt-forming techniques, is greatly restricted. In fact,

-3-

the electrochemical methods are reported to give homogeneous conductive polymer films only to film thickness of about 2000 Å. Powdery deposits are obtained when attempts are made to grow films thicker than this.

- 5 (G. Tourillon and F. Garnier, J. Poly. Poly. Phys. Ed., **22**, 33-39, 1984.)

The unsubstituted polythiophenes form highly conductive complexes on doping which are not stable in normal environments (containing air or water vapor).

- 10 However, electrochemically prepared conductive poly(3-methylthiophene) is environmentally stable.

(G. Tourillon and F. Garnier, J. Electrochem. Soc., Electrochem. Sci. Techn., **130**, 2042-3, 1983.)

- 15 A conductive oligomeric species of poly(thiophene vinylenes), i.e., 6 to 8 repeat units are described in G. Kossmehl et al., Makromol Chem., **131**, 15-54, 1970, and G. Kossmehl, Ber. Bunsenges Phys. Chem., **83**, 417-426, 1979.

- These oligomeric species of poly(thiophene vinylenes) exhibit several undesirable properties, which limit their utility in potential applications such as EMI shielding, and as anti-static materials. For example, the above-cited publications disclose that these oligomeric poly(thiophene vinylenes) are insoluble in common organic solvents which essentially precludes solution processability, are infuseable which essentially precludes melt processability, and exhibit low conductivities on oxidative doping ($10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$) which essentially precludes use of such materials in EMI shielding and circuitry applications.

- 30 Poly(aromatic vinylenes) and poly(heteroaromatic vinylenes) formed from various soluble precursor polymers are known. For example, US Patent No. 4,808,681 and its UK counterpart 8429111 describes various conductive poly(2,5-furanylene vinylenes) and poly(2,5-thienylene vinylenes) which are prepared by heat treatment of sulfonium salt containing precursor polymers resulting in elimination of the sulfide to form the vinylene group. Similarly, Kwan-Yue Jen et al. "Poly(2,5-Thienylene,

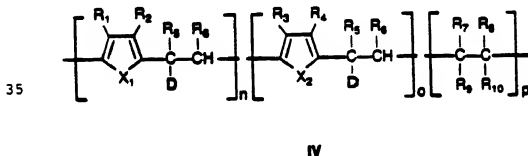
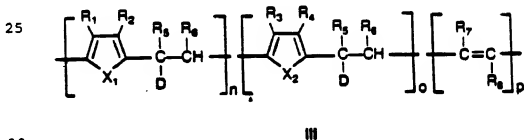
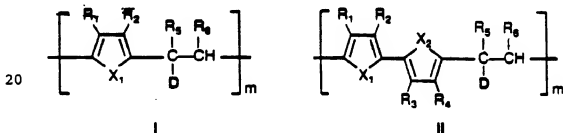
-4-

Vinylene) Prepared Via a Soluble Precursor Polymer", J. Chem. Soc., Chem. Commun., p.309, (1987) describes the preparation of poly(2,5-thienylene vinylenes) from various water soluble polyelectrolytes precursor polymers containing pendant sulfonium groups. The elimination of these groups results in the formation of conjugated unsaturation in the polymeric backbone.

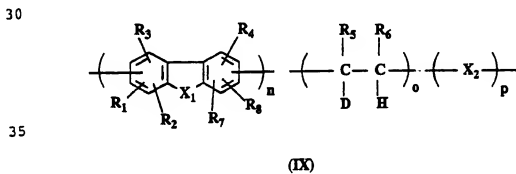
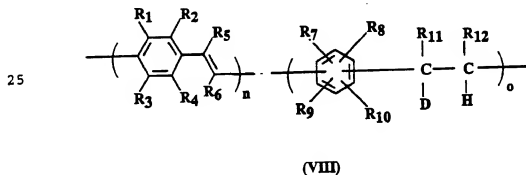
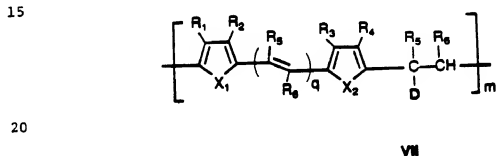
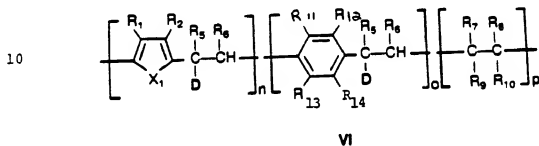
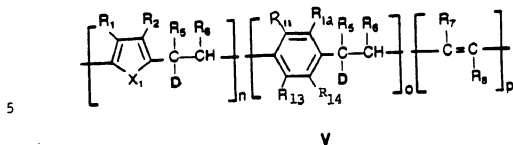
SUMMARY OF THE INVENTION

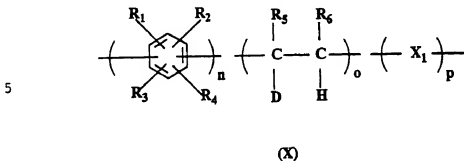
10

One embodiment of this invention relates to homopolymers and copolymers which are useful in the formation of poly(heterocyclic vinylenes), said homopolymers and copolymers comprising recurring units selected from the group consisting of those of the Formulas I to XI:

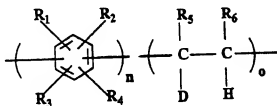


-5-





10



15

(XI)

wherein:

20 m, n, o and p are the same or different and are selected such that m, or the sum of n, o and p is greater than about 20, with the proviso that at least one of n or o is not zero;

q is the same or different at each occurrence and is an integer which can range from 0 to about 4;

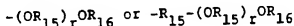
25 D is a leaving group, with the proviso that at least about 1 mole % of D leaving groups based on the total moles of D leaving groups is selected from the group consisting of neutral moieties which on elimination form the anion of a strong non-oxidizing organic or inorganic
30 protonic acid having a pKa equal to or less than about 4 or a species which can be converted into the anion of such an acid such as $-\text{OR}_1$, $-\text{R}_1\text{OCO}_2^-$, F, Cl, Br, I, $-\text{OSO}_2\text{R}_1$, $-\text{OSO}_3\text{R}_1$, $-\text{CO}_2\text{R}_1$, $-\text{OPO}(\text{OR}_1)(\text{OR}_2)$, $-\text{OSiR}_1\text{R}_2\text{R}_3$, and the like, or zwitterionic moieties
35 which on elimination form the anion of such a strong non-oxidizing organic or inorganic acid, protonic acid having a pKa equal to or less than about 4, or a species which can be converted into such an anion such as

-7-

- $-^+NR_1R_2R_3Z^-$, $-P^+R_1R_2R_3Z^-$,
 $-^+SOR_1R_2Z^-$, $-^+SR_1R_2Z^-$,
 $-^+NOR_1R_2Z^-$ and the like where Z^- is an anion of
 a non-oxidizing inorganic or organic protonic acid having
 5 a pKa equal to or less than about 4 or an anionic species
 which can be converted into such an anion such as
 HSO_4^- , F^- , Cl^- , ClO_4^- , Br^- , PO_4^{3-} ,
 ClO_4^- , PF_6^- , NO_3^- , $NR_1R_2SO_3^-$, I^- ,
 SbX_6^- , AsX_6^- , BX_4^- , or PX_6^- where X is a
 10 halogen or $R_1SO_3^-$, or $R_1CO_2^-$ where R_1 , R_2
 and R_3 are the same or different and include groups such
 as hydrogen alkyl, phenyl, phenylalkyl, or alkylphenyl
 which may be unsubstituted or substituted with halogen,
 sulfonic acid or the like such as $CF_3SO_3^-$,
 15 $CH_3SO_3^-$, $H_2NSO_3^-$, $PhNHSO_3^-$,
 $CF_3CF_2CO_2^-$, $CF_3CF_2CF_2CO_2^-$,
 $CF_3(CF_2)_6CO_2^-$, $CF_3CF_2CF_2CF_2CO_2^-$,
 $CF_3CO_2^-$, $CF_3(CF_2)_5CO_2^-$, $CH_3CO_2^-$,
 $CH_3C_6H_4SO_3^-$ and the like or Z^- is said anion
 20 on said anionic species which may be bonded to the
 polymeric backbone of the homopolymer or copolymer by way
 of a divalent moiety such as an alkylene or alkenylene
 group such as $-(CH_2)_3SO_3^-$ or $-(CH_2)_4CO_2^-$;
 R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 ,
 25 R_{10} , R_{11} , R_{12} , R_{13} and R_{14} are the same or
 different at each occurrence and are hydrogen or isotopes
 thereof, hydroxy, amino, alkyl, alkenyl, aryl, alkoxy,
 cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, aryloxy,
 alkylthioalkyl, alkynyl, alkylaryl, arylalkyl, amido,
 30 alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, aryl,
 arylamino, diarylamino, alkylamino, dialkylamino,
 phosphoric acid, alkylaryl amino, arylthio, heteroaryl,
 arylsulfinyl, alkoxy carbonyl, arylsulfonyl, carboxylic
 acid, esters, anhydrides and salts of said acids,
 35 halogen, nitro, cyano, sulfonic acid, or alkyl or phenyl
 substituted with one or more of sulfonic acid, phosphoric
 acid, carboxylic acid, esters, anhydrides and salts of

-8-

said acids, halo, amino, hydroxyl, nitro, cyano or epoxy moieties, or a moiety of the formula:



5

wherein:

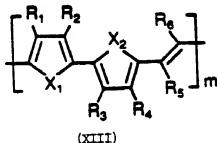
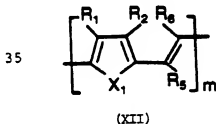
R_{15} is a divalent alkylene moiety having from 1 to about 7 carbon atoms;

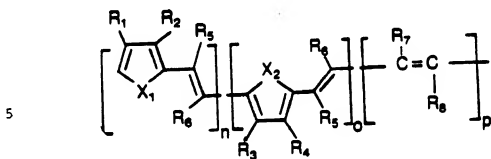
R_{16} is alkyl having from 1 to about 20 carbon atoms; and

r is a natural number from 1 to about 50; or
and R_1 and R_2 , or R_3 and R_4 , or R_5 and R_6 , or R_7 and R_8 , or R_9 and R_{10} , or R_{11} and R_{12} , or R_{13} and R_{14} substituents taken together are
15 an alkylene, alkynylene or alkenylene group completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic or alicyclic carbon ring, which ring may optionally include one or more degrees of unsaturation and divalent heteroatoms of nitrogen, sulfur, sulfinyl, phosphorus, selenium, sulfonyl
20 or oxygen; and

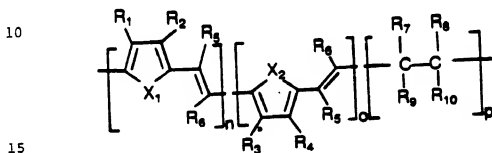
X_1 and X_2 are the same or different and are S, O, Se, NR_{17} , or PR_{17} wherein R_{17} is hydrogen, alkylaryl, arylalkyl, alkyl or aryl, or R_1 .

This invention also relates to solutions of the
25 polymers of Formulas I to XI in protic or aprotic solvents. These solutions thereof can be used to form articles such as films of the polymers of Formula I to XI, which upon subsequent treatment such as heat treatment, or treatment with chemical agents, eliminates "D" to form
30 doped electrically conductive conjugated copolymers and homopolymers having regular or random recurring conjugated units of the following Formulas XII to XXII:



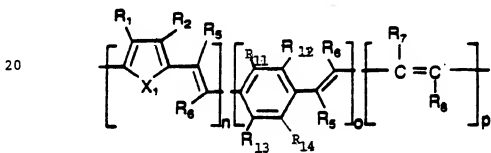


(XIV)



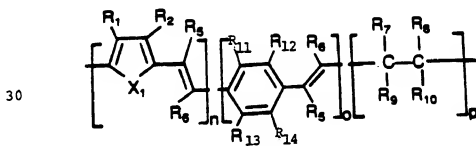
15

(XV)



25

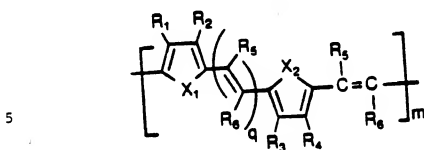
(XVI)



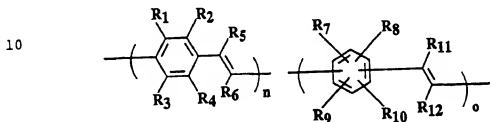
35

(XVII)

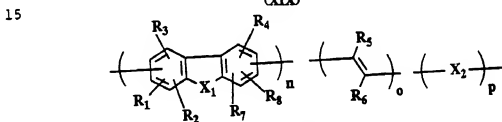
-10-



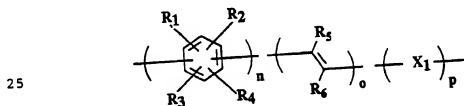
(XVIII)



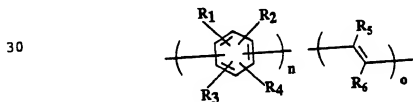
(XIX)



(XX)



(XXI)



(XXII)

35

-11-

wherein m, n, o, p, q, X_1 , X_2 , R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} and R_{17} are as described above, which copolymers and homopolymer are simultaneously doped by the non-oxidizing protonic acid resulting from the elimination of D rendering the copolymer or homopolymer electrically conductive.

Another aspect of this invention relates to a solution which comprises:

- 10 a) an aqueous or organic solvent; and
- b) one or more forms of the copolymers and homopolymers of Formulas I to XI.

Solutions of Formulas I to XI can be conveniently used to form conductive articles by optionally removing the solvent, then inducing elimination of "D" and "H", thereby producing doped electrically conductive polymers of Formulas XII to XXII. The use of the solutions of this invention in the methods of this invention provides conductive article and composites of all shapes, as for example, films and fibers and coatings.

Another aspect of this invention relates to the processing of polymers of the Formulas I to XI and blends of these polymers and conventional thermoplastic and/or thermosetting polymers, i.e., polyolefins, polyesters, 25 polyacrylates, halogenated polyolefins, polyvinyls, such as polyvinyl alcohol, and polyvinyl chloride, polyvinylidene dichloride, polyalkylene oxides, polysiloxanes, polycarbonates, polyamides, and the like to form conductive articles.

Several advantages flow from this invention. For example, this invention provides a simplified thermally activated process for direct formation of conductive doped poly(heteroaromatic vinylenes) and poly(aromatic vinylenes) from non-conjugated precursor polymers without 30 the need for a distinct doping step.

The discovery that non-oxidizing protonic acids dopants render conjugated polymers highly conductive now provides a wide range of new p-type dopants with

-12-

- attributes previously not available. These new protonic acid dopants offer a significant advantage over the previous art (redox dopants) because no by-products are produced by the doping process. In contrast, redox dopants such as FeCl_3 , NOBF_4 , SbF_5 , MoCl_5 and the like, produce a neutral by-product from the doping process (i.e. FeCl_2 , NO , AsF_3 , SbF_3 , MoOCl). Additionally, these new dopants can impart additional desirable properties to doped polymers. In particular, long-chain alkyl or perfluoroalkyl carboxylic or sulfonic acid type dopants can function as plasticizers and can serve to significantly modify the cohesive energy density of doped polymers. With the proper choice of acid dopant, it should be possible to significantly improve the thermal stability, solution and melt processability, and environmental stability of presently known highly conductive polymers.

DETAILED DESCRIPTION OF THE INVENTION

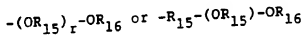
20

One aspect of this invention is a homopolymer or a copolymer comprising recurring monomeric units selected from the group consisting of those of the Formula I to XI, wherein o, q, p, n, m, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , R_{17} , Z^- , D, X_1 and X_2 , are as described above.

- Illustrative of useful R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} , R_{12} , R_{13} and R_{14} groups are hydrogen; cyano; nitro; halo; hydroxyl; amino; alkyl such as methyl, ethyl, butyl, pentyl, hexyl, octyl, nonyl, ~~tert~~-butyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like, alkenyl such as 1-propenyl, 4-butenyl, 1-pentenyl, 6-hexenyl, 1-heptenyl, 8-octenyl and the like; alkoxy such as propoxy, butoxy, methoxy, isopropoxy, pentoxy, nonyloxy, ethoxy, octyloxy, and the like; cycloalkenyl such as cyclohexenyl, cyclopentenyl and the like; alkanoyl such as butanoyl, pentanoyl, octanoyl,

-13-

- ethanoyl, propanoyl and the like; arylamino and diarylamino such as phenylamino, diphenylamino and the like; alkylsulfinyl, alkylsulfonyl, alkylthio, arylsulfonyl, arylthio, and the like, such as butylthio, neopentylthio, methylsulfinyl, benzylsulfinyl, phenylsulfinyl, propylthio, octylthio, nonylsulfonyl, octylsulfonyl, methylthio, isopropylthio, phenylsulfonyl, methylsulfonyl, nonylthio, phenylthio, ethylthio, benzylthio, phenethylthio, sec-butylthio, naphthylthio and
- 10 the like; alkoxy carbonyl such as methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl and the like; alkyl amino and dialkylamino such as dimethylamino, methylamino, diethylamino, ethylamino, dibutylamino, butylamino and the like; cycloalkyl such as cyclohexyl, cyclopentyl,
- 15 cyclooctyl, cycloheptyl and the like; alkoxyalkyl such as methoxymethylene, methoxyethoxyethylene, methoxydiethoxyethylene, ethoxymethylene, butoxymethylene, propoxyethylene, pentoxybutylene and the like; arylalkylamino such as methylphenylamino, ethylphenylamino
- 20 and the like; aryloxyalkyl and aryloxyaryl such as phenoxyphenylene, phenoxyethylene and the like; and various substituted alkyl and aryl groups such as 1-hydroxybutyl, 1-aminobutyl, 1-hydroxylpropyl, 1-hydroxypentyl, 1-hydroxyoctyl, 1-hydroxyethyl,
- 25 2-nitroethyl, trifluoromethyl, 3,4-epoxybutyl, cyanomethyl, 3-chloropropyl, 4-nitrophenyl, 3-cyanophenyl, 1-hydroxy-methyl, and the like; sulfonic acid terminated alkyl and aryl groups, and salts thereof; carboxylic acid and derivatives thereof such as esters, anhydrides and
- 30 salts thereof, and phosphoric acid terminated alkyl and aryl groups, and derivatives thereof such as esters, and salts thereof; such as ethylsulfonic acid, propylsulfonic acid, butylsulfonic acid and sodium salts, phenylsulfonic acid, and the corresponding carboxylic acids, esters and
- 35 anhydrides and salts thereof. Exemplary of other useful R_1 to R_{14} groups are moieties of the formula:



-14-

where r , $-R_{15}$ and $-R_{16}$ are as described above. Useful R_{15} groups include divalent moieties of the formulas $-(CH_2)_2-$, $-(CH_2)_3-$ and $(CH_2C(CH_3)_2)-$, and useful R_{16} groups include $-CH_3$, and $-CH_2CH_3$. Illustrative of substituents having such R_{15} and R_{16} are ethylene glycol monomethylether, diethylene glycol monomethylether, triethylene glycol monomethylether, tetraethylene glycol monomethylether, and the like.

- 10 The nature of the D leaving group may vary widely with the proviso that at least about 1 mole percent of D leaving groups based on the total moles of D leaving groups is a moiety which upon elimination forms a non-oxidizing organic or inorganic protonic acid having a
- 15 pKa equal to or less than about 4, or an acid which can be converted via complexation with Lewis Acids into such an acid. In the preferred embodiments of the invention, at least about 2 mole % of D groups form such an acid, in the more preferred embodiments of the invention, at least
- 20 about 5 mole % of D groups form such an acid, and in the most preferred embodiments of the invention, at least about 10 mole % of D groups form such an acid. The said D groups generate on elimination of said acids having the specified pKa, which may then simultaneously dope the
- 25 polymer of Formula XII to XXII forming the electrically conductive polymer. Generally, useful D groups fall into two general categories or classes of moieties, those which form the required inorganic or organic acid, and those which form species which can be converted into such
- 30 acids. Illustrative of D leaving groups which do not form the required acid but which can be converted into same pseudohalogens such as $-OCN$, $-OR_1$, $-SR_1$, $-OCOR$, $-SeR_1$, $-P(OR_1)_2$, and the like where R_1 is hydrogen or an aliphatic or aromatic group such as alkyl,
- 35 arylalkyl, alkylaryl, alkoxyalkyl, arylalkoxy, and the like. Another class of useful D leaving groups are neutral D groups which on elimination directly form the non-oxidizing inorganic or organic acid. Illustrative of

-15-

- this class of D groups are species such as $-\text{OSO}_2\text{R}_1$, $-\text{CO}_2\text{R}_1$, $-\text{OSO}_3\text{R}_1$, $-\text{OPO}(\text{OR}_1)(\text{OR}_2)$, and halogen where R_1 is as described above, as for example, hydrogen; alkoxyalkyl, such as methoxymethyl, ethoxymethyl, and the like; alkyl such as methyl, ethyl, propyl, and butyl; aryl and alkylaryl such as phenyl, tolyl and the like; arylalkyl such as benzyl, phenethyl, 4-phenyl-butyl and the like; alkanoyl and aroyl such as acetyl, butanoyl, benzoyl, and the like; alkanesulfonyl
- 10 and arylsulfonyl such as methanesulfonyl, ethanesulfonyl, butanesulfonyl, toluenesulfonyl, phenylsulfonyl, and the like; and alkyl or aryl group substituted with carboxylic or sulfonic acid groups or salts thereof such as butylsulfonic acid, butylcarboxylic acid, pentyl sulfonic
- 15 acid; pentyl carboxylic acid, propane sodium sulfonate, pentane sodium sulfonate, and the like.

- Another class of useful D group are zwitterionic species in which the cationic portion can be eliminated as a neutral species, preferably a volatile one, and the
- 20 anionic portion is an anion of a non-oxidizing organic or inorganic protonic acid or is anionic species which can be converted into such an anion. Illustrative of such D groups are species of the formulas: $-\text{SR}_1\text{R}_2$ Z^- , pyridinium, Z^- , $-\text{N}^+\text{R}_1\text{R}_2\text{R}_3$ Z^- , such as
- 25 $-\text{P}(\text{O})\text{R}_1\text{R}_2$ Z^- , $-\text{P}^+\text{R}_1\text{R}_2\text{R}_3$ Z^- , $-\text{N}(\text{O})\text{R}_1\text{R}_2$ Z^- and $-\text{S}(\text{O})\text{R}_1\text{R}_2$ Z , wherein R_1 , R_2 and R_3 are as described above, as for example, alkyl, such as methyl, ethyl, propyl, butyl and the like; alkylaryl, alkoxyaryl, and aryl such as phenyl, tolyl, anisyl, and the like; arylalkyl such as benzyl,
- 30 phenethyl, 4-phenylbutyl, and the like; or R_1 , R_2 , and R_3 together may form an alkenylene or alkylene chain such as $-(\text{CH}_2)_4-$, $-(\text{CH}_2)_3-$, $-(\text{CH}_2)_7-$, $-(\text{CH}_2)_5-$, $-(\text{CH}_2)_6-$, $-\text{CH}=\text{CH}-\text{CH}_2-$, $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$,
- 35 $-\text{CH}_2\text{SCH}_2-$, and $-\text{CH}_2-\text{O}-\text{CH}_2-$, $-\text{CH}_2\text{NH}-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-$, and

-16-

the like or an alkenylene or alkynylene chain having one or more unsaturated moieties completing an alicyclic ring or an aromatic or heteraromatic ring structure;

Z is the anion of a non-oxidizing protonic acid such as

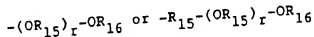
- 5 Cl^- , PO_4^{3-} , CF_3CO_2^- , $\text{CF}_3\text{CF}_2\text{CO}_2^-$, F^- ,
 Br^- , I^- , H_2NSO_3^- , H_2PO_4^- ,
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2^-$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2^-$,
 $\text{CH}_3\text{CH}_2\text{SO}_3^-$, BF_4^- , AsF_6^- , PF_6^- ,
 perfluorooctanoic acid, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$,
 10 CF_3SO_3^- , and the like.

Preferred for use in the practice of this invention are homopolymers, and random or block copolymers of the above Formulas I to XI in which:

- m, n, o and p are the same or different and are
 15 selected such that m, or the sum of n, o and p is an integer at least about 40, with the proviso that at least one of n or o is greater than zero; preferably that the sum of n, o and p, or m is at least about 75;
 q is an integer from 0 to about 4;
 20 R_1 , R_2 , R_3 and R_4 are the same or different at each occurrence and are hydrogen, hydroxyl, halo, amino, cyano, or alkyl having from 1 to about 20 carbon atoms, such as ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, n-pentyl, isopentyl, sec-pentyl,
 25 tert-pentyl, n-hexyl, n-octyl, n-nonyl, n-decyl, and n-dodecyl; phenyl; alkylphenyl such as ,2,4-di-methylphenyl, 4-methylphenyl, 4-ethylphenyl, and 4-butylphenyl; phenylalkyl such as benzyl, phenethyl; alkoxy having from 1 to about 12 carbon atoms such as
 30 methoxy, ethoxy, and butoxy; alkanoyl having from 1 to 20 carbon atoms such as formyl, acetyl, and propenyl; alkylthio having from 1 to 20 carbon atoms such as methylthio, ethylthio, propylthio, dodecylthio and butylthio; alkoxyalkyl having from 1 to 20 carbon atoms
 35 such as methoxymethyl, ethoxyethyl, heptoxypropyl, methoxyethyl, alkenyl having from 1 to about 20 carbon atoms such as allyl, vinyl and 3-butenyl; alkynyl such as ethynyl, propynyl, butynyl; or phenyl and alkyl substituted with

-17-

- hydroxyl, epoxy, sulfonic acid, nitro, cyano, phosphoric acid, carboxylic acid esters, anhydrides, or halo substituents such as trifluoromethyl, 3,4-epoxybutyl, cyanomethyl, 2-nitroethyl, 3-chloropropyl, 4-nitrophenyl,
- 5 $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$; $-\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$; and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$; moiety of the formula:



10 wherein

R_{15} is alkyl having from 1 to about 4 carbon atoms;

R_{16} is alkyl having from 1 to about 10 carbon atoms; and

r is a natural number from 1 to about 25 such as

- 15 ethylene glycol monomethylether, diethylene glycol monomethylether, triethylene glycol monomethylether, tetraethylene glycol monomethylether and the like; or any of R_1 and R_2 or R_3 and R_4 substituents taken together may form an alkylene, alkynylene or alkenylene
- 20 chain having from 2 to 20 carbon atoms completing a 4, 5, 6, 7, 8, 9 or 10 membered ring system which may include one or more heteroatoms of oxygen, nitrogen or sulfur such as 1,4-butanediyl, 1,2-ethanediyl, $-\text{CH}_2\text{SCH}_2-$, $-\text{N}=\text{CH}-\text{CH}=\text{CH}-$, $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$, $-\text{CH}_2\text{OCH}_2-$, $-\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2-$, or $-\text{CH}_2\text{CH}_2-\text{NH}-$.

- 25 R_5 to R_{14} are the same or different at each occurrence and are hydrogen, hydroxyl, halo, amino, cyano, alkyl having from 1 to about 12 carbon atoms, substituted alkyl, phenyl, substituted phenyl, alkylthio having from 1 to about 12 carbon atoms or alkoxy having from 1 to about 12 carbon atoms; alkylamino having about 1 to about 12 carbon atoms or any of R_5 and R_6 , or R_7 and R_8 , or R_9 and R_{10} , or R_{11} and R_{12} , or R_{13} and R_{14} substituents together may form an alkylene chain having 2
- 35 to about 20 carbon atoms completing a 4, 5 or 6 membered ring system which may include one or more heteroatoms of oxygen or sulfur such as 1,4-butendiyl, 1,2-ethanediyl, $-\text{CH}_2\text{SCH}_2-$ $-\text{CH}_2\text{OCH}_2-$; $-\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-$,

-18-

X_1 and X_2 are the same or different and are oxygen, sulfur or $-NR_{17}$ wherein R_{17} is hydrogen or alkyl, or R_1 ;

D is the same or different at each occurrence and is 5 moieties of the formula:

(a) $-OSO_3R_1$, $-OSO_2R_1$, $-OPO(OR_1)(OR_2)$,
 $-NR_1R_1$, $-OCOR_1$, $-OSOR_1$, $-OSO_2NR_1R_2$,
 $-OSONR_1R_2$, or $-OSiR_1R_2R_2$;

10

wherein R_1 and R_2 and R_3 are the same or different at each occurrence hydrogen; alkyl, such as methyl, ethyl, propyl, butyl, hexyl, and octyl; alkanoyl, benzoyl or alkyl or alkoxy substituted benzoyl, such as benzoyl, 15 butanoyl, ethanoyl; phenoxy; alkylphenyl and alkoxyphenyl such as tolyl, anisyl methlphenyl, dodecyl phenyl; and ; alkoxyalkyl such as methoxyethyl; phenylalkyl such as benzyl or phenethyl;

20 (b) F, Cl, Br or I;

(c) $-^+S(O)R_1R_2 Z^-$, and $-S^+R_1R_2 Z^-$ and
 $-^+N(O)R_1R_2 Z^-$,

25 where R_1 and R_2 are the same or different at each occurrence and are alkyl such as methyl, ethyl, or butyl, or R_1 and R_2 together form an alkylene, alkynylene, or alkenylene chain containing one or more unsaturations such as 1,4-butanediyl, 1,3-propanediyl or 1,5-pentanediy 30 completing a saturated or unsaturated ring structure, or an aromatic or heteraromatic ring structure; and

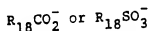
(d) $-N^+R_1R_2R_3Z^-$, and $-P^+R_1R_2R_3Z^-$,

35 where R_1 , R_2 , R_3 are the same or different at each occurrence and are hydrogen, alkyl such as methyl, ethyl, propyl, and butyl; aryl; arylalkyl such as benzyl and phenethyl; alkylaryl and alkoxyaryl such as tolyl and

-19-

anisyl; and alkoxyalkyl such as methoxymethyl; or two or three of R_1 , R_2 and R_3 together may form an alkylene, alkynylene or alkenylene chain having one or more degrees of unsaturation completing a saturated ring structure, such as piperidinium or an aromatic or heterocyclic ring structure such as pyridinium and substituted pyridinium; and

Z^- is an anion such as BX_4^- , SbX_6^- , PX_6^- , AsX_6^- where X is halogen, or a moiety of the formula

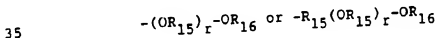


wherein R_{18} is alkyl, or aryl, which may be unsubstituted or substituted with one or more halo, alkyl, alkoxy or aryl groups.

Particularly preferred for use in the practice of this invention are homopolymers or random copolymers of the above-referenced Formula I to XI wherein:

q is an integer from 0 to 3;
m, and the sum of n, o and p are at least about 100 and at least one of n or o is greater than zero.

R_1 , R_2 , R_3 and R_4 are the same or different at each occurrence and are hydrogen; hydroxy; halo; cyano; amino; alkyl having from 1 to about 12 carbon atoms such as ethyl, methyl, propyl, n-butyl, sec-butyl, n-hexyl, n-octyl, and n-dodecyl; phenyl; alkoxy having from 1 to about 12 carbon such as methoxy, nonyloxy, dodecanoxy, ethoxy and butoxy; alkylthio having from 1 to about 12 carbon atoms such as methylthio, ethylthio, propylthio, and butylthio; alkoxyalkyl having from 1 to about 12 carbon atoms such as ethoxymethyl and butoxymethyl; or a moiety of the formula:



-20-

wherein:

R_{15} is alkylene of about 2 to 3 carbon atoms;

R_{16} is alkyl of from 1 to about 3 carbon atoms; and

r is a natural number from 1 to about 10;

5 $R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12},$

$R_{13},$ and R_{14} are the same or different at each

occurrence and are hydrogen; hydroxy; halo; amino; cyano;

alkyl, such as methyl, ethyl or the like; substituted

alkyl such as butylsulfonic acid, propylsulfonic acid,

10 cyanomethyl, epoxybutyl, hydroxy butyl, methyl propyl

carboxylate, pentafluoroethyl, nitropropyl, and

butylcarboxylic acid; alkoxy such as methylthio, ethylthio

and the like; or any of R_5 and R_6, R_7 and R_8, R_9

and R_{10}, R_{11} and R_{12} together may be propylene,

15 butylene or a like divalent alkylene group forming a ring structure ;

Z^- is $AsX_6^-, SbX_6^-, PX_6^-, BX_4^-,$

where X is halogen, or $R_{18}SO_3^-$ or $R_{18}CO_2^-$,

wherein R_{18} is alkyl, phenyl, alkylphenyl or phenylalkyl

20 which may be unsubstituted or substituted with one or more fluoro, chloro, Bromo or cyano groups;

X_1 and X_2 are the same or different and are oxygen, sulfur, or NR_{17} and

D is the same or different at each occurrence and is:

25 a leaving group, with the proviso that at least about

2 mole % of D leaving groups based on the total moles of D

leaving groups on an elimination forms an acid leaving a

pK_a equal to or less than about 4, preferably less than or

equal to about 3, more preferably equal to or less than

30 about 2 and most preferably equal to or less than about

1, or can be converted into such an acid and is selected

from the group consisting of:

(a) $-OSO_2R_1$ and $-R_1CO_2-$ where R_1 is

hydrogen; alkyl such as methyl, ethyl, butyl, and octyl;

35 phenyl; alkylphenyl and alkoxyphenyl such as tolyl and

anisyl; phenylalkyl such as benzyl and phenethyl; and

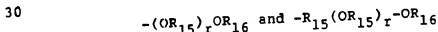
alkanoyl and aryloyl such as acetyl and benzoyl; or

-21-

- (b) $-N^+R_1R_2R_3Z^-$, $-S^+(O)R_1R_2Z^-$,
 $-N(O)R_1R_2Z^-$ or $-S^+R_1R_2Z^-$, wherein R_1 ,
 R_2 and R_3 are aryl such as phenyl; alkyl such as
 methyl, ethyl, and butyl; alkoxyalkyl such as
 5 methoxymethyl; arylalkyl such as benzyl and phenethyl; and
 alkylphenyl and alkoxyphenyl such as tolyl and anisyl; or
 R_1 , R_2 and R_3 together form an alkynylene, alkylene
 or alkenylene chain such as 1,4-butanediyl, 1,5-
 pentanediyl, and 1,5-pent-1,3,5-trienediyl, completing a
 10 ring structure such as tetrahydrothiophenonium;
 pyridinium; and piperidinium; and

- Z^- is AsX_6^- , SbX_6^- , PX_6^- , or BX_4^-
 where X is halogen, or $R_{18}SO_3^-$ or $R_{18}CO_2^-$
 wherein R_{18} is alkyl having from 1 to about 20 carbon
 15 atoms, alkylphenyl having from 7 to about 20 carbon atoms
 or phenyl which may be unsubstituted or substituted one or
 more fluoro, chloro, alkyl, bromo, or cyano, alkoxy or
 sulfonic acid, carboxylic acid, phosphoric acid or
 derivatives thereof (e.g. salts, esters and the like).
 20 Amongst these particularly preferred embodiments,
 most preferred are random copolymers and homopolymers of
 Formula I to XI in which:

- q is an integer from 0 to about 2;
 m, or the sum of n, o and p is at least about 125
 25 R_1 to R_4 are the same or different at each
 occurrence and are hydrogen, hydroxyl, cyano, halogen,
 alkyl having 1 to about 12 carbon atoms, alkoxy having 1
 to about 12 carbon atoms, or alkoxyalkyl having 2 to about
 12 carbon atoms or a moiety of the formula:



wherein:

- R_{15} is $-(CH_2)_2-$ or $-CH_2CH(CH_3)-$;
 R_{16} is $-CH_3$ or $-CH_2CH_3$; and
 35 r is an integer from 0 to 10,
 R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} and R_{12}
 are the same or different at each occurrence and are

-22-

- hydrogen, hydroxy, cyano, amino, alkyl, or any of R_5 and R_6 , R_7 and R_8 , R_9 and R_{10} , R_{11} and R_{12} together may form a divalent alkylene, alkynylene or alkenylene group having from 2 to about 6 carbon atoms
- 5 forming an aromatic or saturated ring;

- D is the same or different at each occurrence and is:
- a leaving group, with the proviso that at least about 2 mole % of D leaving groups based on the total moles of D leaving groups on an elimination forms an acid having a
- 10 pKa equal to or less than about 4.0, preferably less than or equal to about 3, more preferably equal to or less than about 2 and most preferably equal to or less than about 1, or can be converted into such an acid and is selected from the group consisting of:

15

O

- (a) $-S^+R_1R_2Z^-$ or $-S^+R_1R_2Z^-$ wherein R_1 and R_2 are the same or different at each occurrence and are hydrogen; alkyl such as methyl, ethyl, propyl, and
- 20 butyl; aryl such as phenyl; or R_1 and R_2 together may form an alkylene, alkynylene, or alkenylene chain and

O

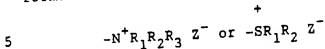
- (b) $-N^+R_1R_2R_3Z^-$, or $-NR_1R_2^+Z^-$
- 25 wherein R_1 , R_2 , R_3 are alkyl such as methyl; ethyl; and butyl; benzyl; phenyl; phenethyl; or two or more of R_1 , R_2 and R_3 together may form an alkylene, alkynylene, or alkenylene chain such as 1,4-butanediyl, 1,5-pentanediyl, and 1,5-pent-1,3-dienediyl completing a
- 30 saturated cyclic structure or an unsaturated aromatic or heteroaromatic structure such as pyridinium; and

- (c) Z^- is of the formula $R_{18}SO_3^-$ or $R_{18}CO_2^-$, wherein R_{18} is alkyl having from 1 to about 20 carbon atoms which may be substituted with one or
- 35 more halogen groups or, alkylphenyl having from 7 to about 20 carbon atoms; and

- (d) X_1 and X_2 are sulfur, or $-NH-$ or $-NR_{17}-$.

-23-

Especially good results are provided in those embodiments of the invention where D is a moiety of the formula:



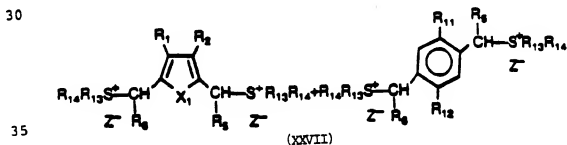
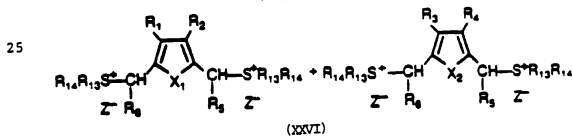
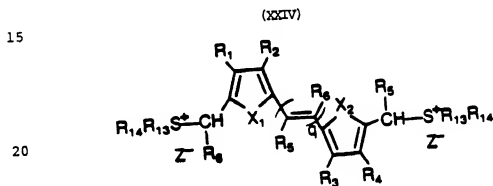
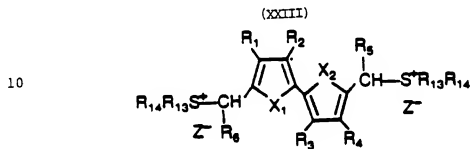
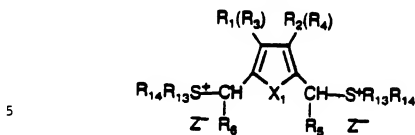
wherein R_1 , R_2 , R_3 and Z^- are as described above.

This invention also relates to solutions of the homopolymers and copolymers of Formula I to XI comprised of one or more of said copolymers and homopolymers and a protic and/or an aprotic solvent. Useful solvents as can vary widely and include such solvents as water, ethanol, methanol, butanol, propanol, acetone, toluene, hexamethyl phosphoric triamide, dimethylformamide, dimethylacetamide, methylene chloride propylene carbonate, sulfolane and the like, or mixtures thereof.

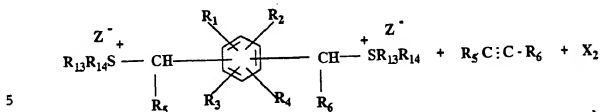
The solvent chosen for use in any particular situation will usually depend on the nature of the various substituents. For example, the more polar the particular substituents, the more polar the solvent; and conversely, the less polar the substituent the less polar the solvent. In the preferred embodiments of this invention, solvents are selected from the group consisting of water, methanol, butanol, ethanol, propanol, sulfolane, dimethyl sulfoxide, methylene chloride, dimethylformamide, N-methyl pyrrolidinone and mixtures thereof, and in the particularly preferred embodiments of the invention, the solvent is selected from the group consisting of water, sulfolane, methanol, butanol, and dimethyl formamide and mixtures thereof. Particularly preferred is water.

The copolymers and homopolymers of Formulas I to XI can be conveniently prepared in a one or two step procedure. In the first step, polymers of the Formula I to XI in which D is $-N^+R_1R_2 \quad Z^-$ are formed. In this step, a compound or group of compounds, whichever is applicable, of the following Formulas XXIII to XXXIII:

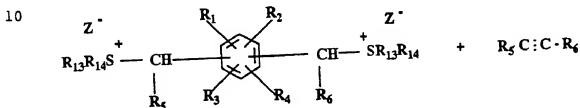
-24-



-26-



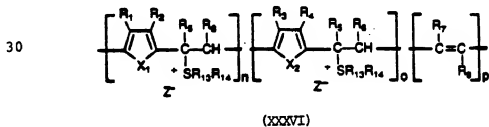
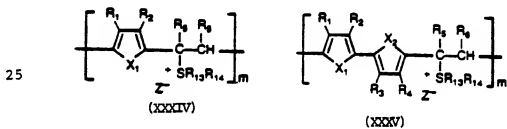
(XXXII)



15

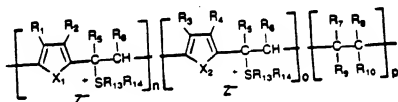
(XXXIII)

20 is treated with one mole equivalent of base to form polymers of the Formula XXXIV to XLIV:

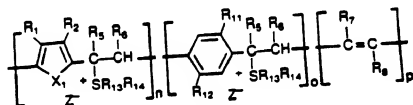


35

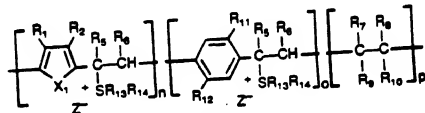
-27-



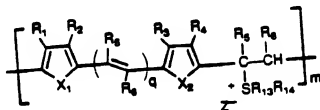
(XXXVII)



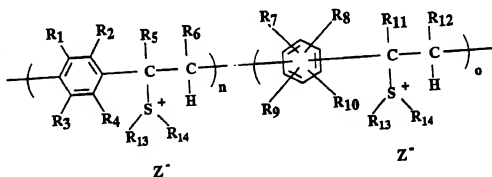
(XXXVIII)



(XXXIX)

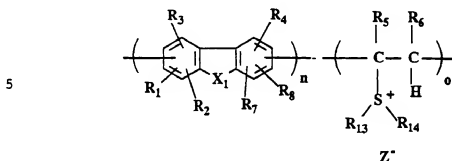


(XL)



(XLI)

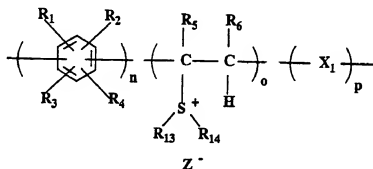
-28-



(XLII)

10

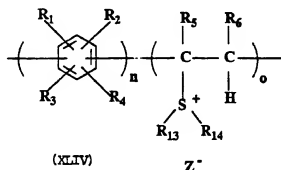
15



(XLIII)

20

25



(XLIV)

In general, this reaction is carried out in solution using the protic or aprotic solvents described above. Bases for use in this reaction are not critical and the only requirement being that the base is active in the solvent in which the reaction is being conducted. Illustrative of useful bases are alkali metal hydroxides such as sodium hydroxide, lithium hydroxide, and potassium hydroxide; alkali metal carbonates and bicarbonates such as sodium carbonate, sodium bicarbonate, potassium carbonate, and potassium bicarbonate; organic amine containing bases such as piperidine, pyridine, DABCO, ethylene diamine,

- tripropylamine, tributyl amine, and the like; alkali metal alkoxides such as potassium *t*-butoxide, lithium methoxide, lithium ethoxide, sodium methoxide, sodium ethoxide, potassium methoxide, and potassium ethoxide; water
- 5 insoluble bases such as calcium oxide, Barium oxide, magnesium oxide and the like; and polymeric bases such as poly(*p*-amino styrene), basic forms of ion exchange resins such as Amberlyst and amberlyte resins in OH⁻ form or free base forms. Preferred bases are sodium hydroxide, lithium
- 10 hydroxide, potassium hydroxide, sodium methoxide, sodium ethoxide, potassium *t*-butoxide and sodium carbonate, and particularly preferred bases are sodium hydroxide, lithium hydroxide, potassium hydroxide, sodium methoxide, and sodium ethoxide. Amongst these particularly preferred
- 15 embodiments, most preferred are those embodiments of the invention in which the base is sodium hydroxide, potassium hydroxide, lithium hydroxide, and sodium methoxide.

- As noted above, solvents for use in this process are those in which the polymers of Formulas XXXIV - XLIV are
- 20 soluble and can vary widely. Preferred solvents are water, methanol, ethanol, butanol, dimethylsulfoxide, acetone, sulfolane, dimethylformamide, N-methylpyrrolidone and acetonitrile, and particularly preferred solvents are water, methanol, ethanol, dimethylformamide, and
- 25 N-methylpyrrolidone. Amongst those particularly preferred solvents, most preferred solvents are methanol, ethanol, dimethylformamide and water.

- Reaction temperatures are not critical and can vary widely. In general, the polymerization reaction is
- 30 carried out at a temperature of from about -15°C to about 200°C. In the preferred embodiments, reaction temperature of from about -15°C to about 50°C, and in the particularly preferred embodiments reaction temperatures are from about -5°C to about 25°C.
- 35 Reaction pressures are not critical and the reaction can be carried out at sub-atmospheric pressure, atmospheric pressure and super-atmospheric pressure. For

-30-

convenience, the reaction is carried out at atmospheric or autogeneous pressure.

Reaction times can vary widely. In general, the reaction is carried out over a period of from about a few seconds to a few hours.

In the second step of the process, those polymers of the Formulas I to XII in which D is other than $^{-+}\text{SR}_1\text{R}_2\text{Z}^{-}$, or those in which D is a mixture of $^{-+}\text{SR}_1\text{R}_2\text{Z}^{-}$ with various other permissible D groups are formed from polymers of the Formulas XXXIV to XLIV. In this step, solutions of polymers of the Formulas XXXIV to XLIV are treated with various agents or mixtures thereof to convert all or a portion of the $^{-+}\text{SR}_1\text{R}_2\text{Z}^{-}$ groups into other permissible D groups or mixtures of $^{-+}\text{SR}_1\text{R}_2\text{Z}^{-}$ and other permissible D groups. Useful agents may vary widely and depends on the nature of the D moiety. Illustrative of useful agents are species of the formula:

(a) MOSO_2R_1 , MCO_2R_1 and MOSO_3R_1 where M is hydrogen or a metal ion and R_1 is as described above such as alkyl, aryl, arylalkyl, alkylaryl and the like. Illustrative of suitable compounds are sodium toluene sulfonic acid, potassium methyl sulfonic acid, sodium trifluoroacetic acid, sodium acetate, potassium benzoate, and the like.

(b) $\text{NR}_1\text{R}_2\text{R}_3$ where R_1 , R_2 and R_3 are the same or different at each occurrence and are as described above such as hydrogen, alkyl from 1 to about 20 carbons aryl, alkylaryl or arylalkyl, or R_1 , R_2 , R_3 form an alkylene, alkenylene or alkynylene chain completing a monocyclic, bicyclic, alicyclic, aromatic or heteroaromatic ring system. Illustrative of suitable $\text{NR}_1\text{R}_2\text{R}_3$ compounds are triethylamine, ethylamine, diethylamine, cyclohexylamine, benzylamine, 1-phenylethylamine, tri-propylamine, methylaniline, diphenylamine, pyrazole, imidazole, oxazole, thiazole, or heterocyclic compounds such as pyridine, 1,2-dihydroquinoline, methylethylamine,

-31-

benzyldimethylamino, N,N-dimethylaniline, trimethylamine, dimethylethylamine, piperidine, 5,6-benzoquinoline, N-methyl piperidine, pyrrolidine, picoline, quinoline, isoquinoline, pyrrole, carbazole, purine, purimidine, morpholine, and the like.

(c) $PR_1R_2R_3$, wherein R_1 , R_2 and R_3 are the same or different at each occurrence and are as described above such as alkyl from 1 to about 20 carbons, aryl alkylaryl, arylalkyl, alkoxy from 1 to about 20 carbons, aryloxy, alkylaryloxy or arylalkyloxy. Illustrative of such compounds are diphenylethyl phosphine, triphenyl phosphine, triethylphosphine, benzyl dimethyl phosphine, phenethoxy diethylphosphine, triphenoxyphosphine, triphenylphosphine, tri- (4-tolyl) phosphine, and the like.

(d) MX wherein M is a metal ion and X is OH^- , OR_1^- , Cl^- , F^- , Br^- and I^- . Illustrative of these materials are sodium iodide, sodium chloride, lithium fluoride, sodium bromide, sodium hydroxide, sodium ethoxide and the like.

OH

(e) R_1NR_2 wherein R_1 and R_2 are the same or different and are alkyl having from 1 to about 10 carbon atoms, or aryl, alkylaryl, or arylalkyl having from about 6 to about 20 carbon atoms, or R_1 and R_2 together may form a cyclic structure. Illustrative of these materials are N,N-dimethyl hydroxyl amine, N,N-diethyl hydroxyl amine, N-phenyl-N-methyl hydroxyl amine, 1-hydroxypiperidine and the like.

(f) R_1OH wherein R_1 is hydrogen, alkyl, aryl, alkoxyalkyl, alkylaryl, arylalkyl, and the like as described above.

Although we do not wish to be bound by any theory, we believe that these agents function in certain cases as nucleophiles to displace the labile sulfonium groups in polymers of Formulas I to XI which contain the other D groups.

-32-

By judicious choice of agent or agents, reaction solvent and reaction time, the properties of polymers of Formulas I to XI can be tailored to meet desired processing conditions, film forming properties, and morphology of the desired conjugated polymers of Formulas XII to XXII.

Particularly preferred agents are those of the formula:

MOSO_2R_1 , MOSO_3R_1 and $\text{R}_1\text{CO}_2\text{M}$ wherein M is hydrogen or a metal ion, and R_1 is alkyl of 1 to about 20 carbons, fluorinated alkyl, alkylphenyl, alkoxyphenyl, phenyl, or benzyl;

$\text{NR}_1\text{R}_2\text{R}_3$, wherein R_1 , R_2 and R_3 are the same or different at each occurrence and are hydrogen, alkyl of 1 to about 20 carbons, phenyl or alkylphenyl, alkoxyphenyl or phenylalkyl having from about 6 to about 20 carbon atoms or R_1 , R_2 , R_3 taken together may form an alkylene, alkynylene or alkenylene chain which may form a monocyclic or bicyclic or alicyclic or aromatic ring structure of from about 6 to about 20 carbon atoms such as pyridine; and

$\text{PR}_1\text{R}_2\text{R}_3$, wherein R_1 , R_2 and R_3 are alkoxy, aryloxy, alkylaryloxy, arylalkyloxy or alkyl.

Most particularly preferred agents are pyridine, trimethylamine, triethylamine, tributylamine, quinoline, tributylphosphine, trimethylphosphine, triethylphosphine, triphenylphosphine, 4-dimethylamino-pyridine and the like.

In those embodiments of this invention where D is zwitterionic, Z^- moieties can be totally or partially changed through use of standard ion exchange techniques. Such techniques are well known to those of skill in the art and will not be described herein in any great detail. Such exchanges may be carried out for a number of purposes, for example, to modify the solubility characteristics of a polymer, to modify the conductivity characteristics of the conjugated backbone polymer resulting from elimination of the D group.

Another aspect of this invention relates to a process for preparing conductive polymers from conjugated backbone copolymers and homopolymers of the Formulas XII to XXII which are prepared from the corresponding polymers of the Formula I to XI. In general, these neutral conjugated backbone polymers are prepared by thermal treatment of the precursor polymers of Formulas I to XI, either as solutions or in the solid state as precast or prefabricated articles. Generally, useful temperatures may range from about -10°C to about 300°C . The thermal treatment eliminates D in two ways, as DH or as D and HZ. Useful temperatures depend on the structure of the polymer, the nature of D and the nature of Z^{-} , if present, and may vary widely. Temperatures which are generally useful can be determined by routine experimentation. The elimination of D forms one of two acidic species of DH and HZ, D and Z have been selected such that the conjugated backbone polymer formed by the elimination of D is spontaneously doped by the acidic species after elimination of D.

Chemical methods can also be used to convert prepolymers I to VII into conjugated polymers of Formulas VIII to XIV. In these chemical methods, the precursor polymers of Formulas I to VII, either in solution or in the solid state, are treated with a chemical agent which causes elimination of D. For example, a Lewis acid can be used to form a protonic acid doped conjugated polymer from a precursor non-conjugated polymer by a Lewis-acid-catalyzed elimination reaction. Useful Lewis acids are AsX_3 , SbX_3 , PX_3 , BX_3 , AlX_3 (where X is halogen), and the like. Illustrative of such a system is poly(2,5-dibutoxyphenylene-1,4-diyl-1'-acetoxy ethylene-1',2'-diyl), which can be converted into protonic acid doped and conductive poly(2,5-dibutoxyphenylene vinylene) by treatment with BF_3 which induces elimination of acetic acid which forms a new stronger protonic acid, $\text{H}^+\text{BF}_3\text{OAc}^-$, that dopes the conjugated polymer.

- It can be appreciated that mixtures of protonic acids, or mixtures of protonic acids and Lewis acids capable of inducing acid-catalyzed polymerization of suitable monomers in a suitable solvent or in pure liquid monomer can give conducting polymer composites in non-conducting host polymers by *in-situ* polymerization of the monomer in the presence of a conjugated polymer. Illustrative of useful monomers are those which polymerize by ring opening reactions. Such monomers include cyclic ethers, such as ethylene oxide, propylene oxide, epichlorohydrin, oxetanes, 3,3-bis(chloromethyl) oxetane, tetrahydrofuran, oxepane, or a mixture of tetrahydropyran and other cyclic ethers, and the like; cyclic ethers containing more than one oxygen, such as 1,3-dioxolanes, 1,3-dioxanes, 1,3-dioxepanes, 1,3-dioxocanes, 1,3-dioxonanes, 1,3-dioxacycloundecanes, 1,3-dioxacyclotridecane, 1,3,5-trioxanes, 1,3,5-trioxepanes, 1,3,6-trioxocanes, 1,3,5,7-tetraoxanes, 1,3,6,9-tetraoxacycloundecanes, 1,3,6,11-tetraoxacyclotridecane, 1,3,6,9,12-pentaoxacyclotetradecanes, 1,3,6,9,12,15-hexaoxacycloheptadecanes, and the like; cyclic sulfides, such as thiacyclopropane, thiacyclobutane, and the like; lactams, such as 3-ethanolactam, 3-propanolactam, 4-butanolactam, 5-pentanolactam, 6-hexanolactam, 7-heptanolactam and the like; lactones, such as γ -propiolactone, γ -butyrolactone, γ -butyrolactone, γ -valerolactone, γ -caprolactone, and the like. Other lactones analogues, such as glycolides, lactides, ethylene carbonate, 1,3-dioxepane-7-ones, 1,5-dioxepane-7-ones, 1,4-dioxepane-7-ones, 1,4-dioxane-2-ones, ethylene oxalate, dioxane-2,6-diones, 1,4-thioxane-3-ones, thioxepane-2-ones, and the like; bicyclic acetals, such as 2,7-dioxabicyclo [2.2.1]heptane, 6,8-dioxabicyclo[3.2.1]octane, 2,7-dioxabicyclo[4.1.0]heptane, 2,6-dioxabicyclo[3.1.1]heptane, 2,8-dioxabicyclo[3.2.1]octane, and the like; cyclic siloxanes, such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane,

-35-

hexaalkylcyclotrisiloxane, octaalkyltetrasiloxane, and the like; and cyclic amines such as aziridine, azetidine, conidine, 1-azabicyclo[2.2.2] octane, 1,4-diazabicyclo-[2.2.2]octane, and the like. Illustrative of such a
5 system is a solution of poly(3-methoxythienylene vinylene) in tetrahydrofuran (THF) to which has been added pentafluoropropionic acid in a sufficient amount so as to dope the conjugated polymer and cause acid-catalyzed polymerization of THF. Upon removal of residual THF from
10 the composite solution, a conductive composite film comprised of protonic acid doped poly(3-methoxythienylene vinylene) and poly(tetrahydrofuran) is obtained.

Useful Lewis acids are those mentioned above. The conductive polymer solutions used can be either a true
15 solution or a suspension. The polymer can be either a conjugated polymer or a non-conjugated precursor polymer which is capable of acid-catalyzed transformation into its conjugated form.

The electrically conductive forms of the polymers of
20 Formulas XII to XXII are formed by the elimination of D from polymers of Formulas I to XI. The level of conductivity may vary widely and is such that the conductivity is at least about $10^{-8} \text{ohm}^{-1} \text{cm}^{-1}$. The upper conductivity is not critical, and usually the
25 highest conductivity which can be obtained is provided. In the preferred embodiments of the invention, the conductivity is equal to or greater than about $10^{-4} \text{ohm}^{-1} \text{cm}^{-1}$, and in the more preferred embodiments of the invention, the conductivity is equal to or greater
30 than about $10^{-2} \text{ohm}^{-1} \text{cm}^{-1}$. In the most preferred embodiments of the invention, the conductivity is equal to or greater than about $10^{-1} \text{ohm}^{-1} \text{cm}^{-1}$.

As noted above, this invention also relates to solutions of the polymers of Formulas I to XLIV. The
35 solvent type employed can vary widely, from polar to non-polar. Useful solvents include water and various organic solvents. In general, solvents which can be used in the practice of this invention will have a dipole

-36-

- moment greater than zero and less than or equal to about 5, and a dielectric constant of less than about 190. Illustrative of useful solvents are water, alcohols, such as methanol, ethanol, propanol, trifluoroethanol, benzyl alcohol, butanol and the like, amines such as triethylamine, tributylamine, diethylamine, pyridine, and the like, acids such as trifluoroacetic, acetic, formic, methane sulfonic, sulfuric and trifluoromethane sulfonic acids; anhydrides such as acetic anhydride, trifluoroacetic anhydride, propionic anhydride and the like, sultones, such as propane sultone, butane sultone, pentane sultone and the like; alkyl alkanesulfonates such as methyl methanesulfonate, ethyl methanesulfonate, butyl methanesulfonate, propyl ethanesulfonate and the like;
- 15 linear and cyclic ethers such as 1,2-dimethoxyethane, dimethoxymethane, dioxane, glymes, diglymes, tetrahydrofuran, 2-methyltetrahydrofuran, anisole, diethylether and the like; nitriles such as acetonitrile, propionitrile, butyronitrile, benzonitrile and the like;
- 20 hydrocarbons such as cyclohexane, pentane, hexane and cyclopentane; halocarbons such as carbon tetrachloride, dichloromethane, dichloroethylene, and 1,2-dichloroethane, trichloroethylene; aromatic solvents such as benzene, toluene, xylene, nitrobenzene and the like; ketones such as 4-methyl-pentanone, methylethylketone, acetone, and the like;
- 25 carbonates such as propylene carbonate, dimethyl carbonate, ethylene carbonate and the like; esters such as methyl formate, methyl acetate, γ -butyrolactone, ethyl acetate and the like; nitroalkanes, such as nitromethane, nitroethane, nitropropane, and the like; amides such as N-ethyl formamide, N-ethyl acetamide, dimethyl formamide, dimethyl thioformamide, N,N-dimethyl acetamide, N-methylpyrrolidinone and the like; organophosphorus compounds such as hexamethyl phosphorous triamide,
- 35 diethylphosphate, triethylphosphate, trimethylphosphate and the like; and organosulfur compounds such as sulfolane, methyl sulfolane, dimethyl sulfone, dimethyl sulfoxide, dimethyl sulfolane, glycol sulfite,

-37-

tetraethylsulfamide and the like. Mixtures of such solvents can also be used as for example mixtures of sulfolane and acetonitrile, or water and methanol.

- The solvent or solvent mixture selected for use in any particular situation will depend primarily on the polarity of various $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, P_1, R_2, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}$ and/or R_{17} substituents, and/or the state of the polymer, i.e. eliminated or uneliminated. In general, more polar compositions will require solvents with higher dielectric constants and dipole moments (within the above specified range). Conversely, less polar compositions will require solvents with lower dielectric constants and dipole moments (within the above specified ranges).

- In general, solvents chosen for use with polymers having relatively polar substituents will usually have a dipole moment of from about 0.3 to about 5.0, preferably from about 1.8 to about 5.0; and a dielectric constant of from about 10 to about 190, preferably from about 20 to about 100. Illustrative of such solvents are alcohols, such as methanol, ethanol, isopropanol, and the like; linear and cyclic ethers, such as tetrahydrofuran, tetrahydropyran, 2-methyltetrahydrofuran, diethylether, diglyme, glyme and the like; halocarbons such as chloroform, 1,2-dichloroethane, dichloromethane and the like; amides, such as dimethylformamide, N,N-dimethylacetamide, N-methyl pyrrolidone and the like; substituted aromatics, such as xylene, anisole, toluene and the like; nitriles, such as acetonitrile, propionitrile, benzonitrile, butyronitrile, and the like; sulfoxides and other sulfur containing solvents such as dimethylsulfoxide and the like; nitro substituted alkanes and aromatics such as nitromethane, nitropropane, nitrobenzene and the like; and carbonates such as propylene carbonate, ethylene carbonate and the like, and water or mixtures thereof.

-38-

In general solvents chosen for use with polymers having relatively non-polar substituents will have a dipole moment of from about 0 to about 3.0, preferably from about 0 to about 2.5; and a dielectric constant of
5 from about 2.0 to about 50, preferably from about 2.0 to about 35. Illustrative of such solvents are halocarbons such as dichloromethane, and the like; aromatic solvents such as toluene, xylene, benzene and the like; cyclic and linear ethers such as dimethoxyethane, tetrahydrofuran and
10 the like; esters such as ethylacetate, methyl formate and the like; sulfoxides, such as dimethylsulfoxide and the like; cyclic and linear amides, such as dimethylformamide, N-methylpyrrolidone, N,N-dimethylacetamide and the like; and ketones such as acetone and the like and mixtures
15 thereof.

In general, the amount of solvent as a proportion of the amount of solution is not believed to be critical, since any amount as a liquid will form at least a viscous gel with doped or undoped polymers. These viscous
20 embodiments of the invention may be particularly useful for silkscreening, extruding fibers, and for applying thick film coatings on substrates. For other applications, it may be preferred, however, to use sufficient liquid solvent to lower the viscosity of the
25 gel or solution to a point where it flows at least sufficiently to conform to a container shape or mold or set up as a coating in a reasonable short period of time, e.g., in 30 minutes or less. Preferably, the solvent is present in sufficient amounts to lower the viscosity of
30 the solution to less than about 2,000 centipoise, and more preferably from about 1 to about 1000 centipoise.

In addition to the essential copolymer or homopolymer and solvent, whichever is applicable, the solutions of this invention can include other optional ingredients and
35 mixtures thereof which either dissolve or do not dissolve in the solution. The nature of such optional ingredients can vary widely, and include those materials which are known to those of skill in the art for inclusion in

polymer articles. In the case of dissolvable components, materials may be present which alter the physical or mechanical properties of either the solution or the articles eventually cast from the solution. Examples of such materials include other conventional polymers such as polyacrylonitrile, polyvinylidene chloride, polyethylene oxide, polystyrene, nylon, polyvinylsulfonic acid, cellulose acetate butyrate, polypropylene, polyethylene, cellulose acetate, polyphenylene oxides, polycarbonates, polyacrylates, and the like. In the case of nonsoluble components, materials may be present which either fill or form a substrate for the conductive polymer cast from the solution. These non-soluble components include other polymers such as polyacetylene which may become conductive upon doping, graphite, carbons, metal conductors, reinforcing fibers and inert fillers (such as clays and glass).

The method of forming the solutions of this invention is not critical and can vary widely. For example, the solution of this invention can be prepared merely by dissolving the desired amount of the polymer in a solvent in which it is soluble such as water, toluene or nitrobenzene. Or, solutions can be formed by directly polymerizing the monomers and/or eliminating D from polymers in the solvent.

Various methods are contemplated for using the solution of the present invention. For example, it is contemplated to remove the solvent from the solution to allow the copolymer or homopolymer to solidify. The solvent can be removed from the solution through use of any conventional solvent removal method but is removed preferably by evaporation. Alternatively, the solvent can be removed by extraction with an extractant in which the solvent is substantially more soluble than the polymer.

As will be appreciated by those skilled in polymer processing, the ability to form polymer articles by removing a solvent from a solution enables one to prepare articles of a wide variety of shapes and sizes. Thus, for

-40-

example, by removing volatiles from the present solution spread on a surface, films and coatings of any desired thickness can be prepared. By extruding the solution through a die, fibers or films can be made. Similarly, by removing volatiles from the solution in a mold of various shapes, shaped articles conforming in shape to the mold can be prepared. It will be appreciated that some shrinkage might occur between the solution in its last flowable state to the final article, but such shrinkage is conventionally accounted for in molding polymers from solution. It is also contemplated that, once a solution is formed, a partial or substantial removal of solvent will occur prior to placing the solution on a surface or in a mold, with the final venting of solvent occurring on the surface or in the mold. It is contemplated that, if additional soluble components are introduced into the solution, they will, unless also volatile, be present in the shaped article formed. If the fourth component is a non-volatile liquid, then the removal of volatile components may leave a new liquid or plasticized form of doped conducting polymer or neutral polymer. If the additional components are volatile, then foamed or expanded cellular forms of the polymer may be formed.

The polymers of Formula I to XI or blends of such polymers and one or more thermoplastic polymers can also be melt processed into useful articles using conventional melt processing techniques. For example, if a blend is used, the various components are granulated, and the granulated components mixed dry in a tumbler, Banbury mixer or other suitable mixer. The components of the blend are usually mixed until the blend is uniform or as homogenous as possible. The blend is then heated above the melting point of at least one of the polymeric components preferably with mixing. Such treatment may cause elimination of D and formation of conductive polymers XII to XXII as a conductive blend with one or more thermoplastic polymers. For example, the blend may be conventionally melted by heating in a conventional

-41-

extruder. As will be appreciated by those of skill in polymer processing, the ability of a polymer to be melt processed allows for the manufacture articles of a wide variety of shapes merely by placing the melt in a mold of the desired shape and cooling the melt below the melting point of at least one of the polymer components. For example, by spreading a melt on a surface and cooling, films of any desired thickness can be fabricated. Similarly fibers and films can be made by extruding the melt through a suitable die, and shaped articles can be formed by placing a melt into a mold having the desired shape and cooling the melt below the melting point of one or more of the polymeric components.

The polymers of Formulas I to XXII can be fabricated alone or as blends with one or more thermoplastic polymers. Useful thermoplastic polymers may vary widely. Illustrative of useful polymers are those formed by polymerization of unsaturated monomers such as polypropylene, polyethylene, poly(octadiene), polyisobutylene, poly(pentene), poly(styrene), poly(2-methylstyrene), poly(4-methylstyrene), poly(hexene), poly(methylhexene), poly(butylene), poly(methylpentene), poly(4-methylpentene), poly(vinyl-cyclopentane), poly(vinylcyclohexane), poly(vinylnaphthalene), poly(vinylchloride), poly(vinyl fluoride), poly(vinylidene fluoride), poly(vinyl alcohol), poly(acrylonitrile), poly(vinyl acetate), poly(vinylmethylether), poly(methylacrylate), poly(methylmethacrylate), acrylonitrile-butadiene-styrene copolymer, polyacrylamide, and the like. Also illustrative of useful thermoplastic polymers are polyamides and polyesters such as the copolyamides of 30% hexamethylene diammonium isophthalate and 70% hexamethylene diammonium adipate, the copolyamide of up to 30% bis(4-aminobutyric acid) (nylon 4), poly(4-aminohexanoic acid) (nylon 6), poly(6-aminocaproic acid) (nylon 6,6), poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6,10),

- poly(heptamethylene pimelamide) (nylon 7,7),
poly(octamethylene suberamide) (nylon 8,8),
poly(hexamethylene sebacamide) (nylon 6,10),
poly(nonamethylene azelamide) (nylon 9,9),
5 poly(decamethylene azelamide) (nylon 10,9), poly(decamethylene sebacamide) (nylon 10,10), poly[bis(4-amino-cyclohexyl)methane-1,10-decanedicarboxamide], poly(m-xylylene adipamide), poly(p-xylylene sebacamide),
poly(2,2,2-trimethylhexamethylene tere-phthalamide),
10 poly(piperazine sebacamide), poly(metha-phenylene isophthalamide) (Nomex), poly(p-phenylene terephthalamide) (Kevlar), poly(11-amino-undecanoic acid) (nylon 11),
poly(12-aminododecanoic acid) (nylon 12),
polyhexamethylene isophthalamide, polyhexamethylene
15 terephthalamide, poly(9-aminononanoic acid) (nylon 9),
polycaproamide, poly(ethylene terephthalate), poly(cyclohexylenedimethylene, terephthalate), poly(ethylene dodecate), poly(butylene terephthalate), poly[ethylene(2,7-naphthalate)], poly(methaphenylene isophthalate), poly-
20 (glycolic acid), poly(ethylene succinate), poly(ethylene adipate), poly(ethylene sebacate), poly(decamethylene azelate), poly(decamethylene azipate), poly(decamethylene sebacate), poly(dimethylpropiolactone), poly(para-hydroxybenzoate) (Ekonol), poly(ethylene oxybenzoate)
25 (A-tell), poly(ethylene isophthalate), poly(tetramethylene terephthalate), poly(hexamethylene terephthalate), poly-(decaethylene terephthalate), poly(1,4-cyclohexane dimethylene terephthalate) (trans), poly(ethylene 1,5-naphthalate), poly(ethylene 2,6-naphthalate), poly(1,4-
30 cyclohexylidene dimethylene terephthalate) (Kodel)(cis),
poly(1,4-cyclohexylidene dimethylene terephthalate) (Kodel)(trans), poly(phenyl sulfide), poly(phenylene oxide), poly(carbonates) such as poly[methane bis(4-phenyl) carbonate], and poly[2,2-propane bis(4-phenyl) carbonate].
35 This invention has many uses. For example, the conductive polymers of this invention can be used in the fabrication of conductive articles such as housings for sensitive electronic equipment as for example

-43-

microprocessors; infrared, radio wave, and microwave absorbing shields; flexible electrical conducting connectors; antistatic coatings; conductive bearings and brushes and semiconducting photoconductor junctions. It is contemplated that the conductive solutions of this invention will be used in the fabrication of the articles of this invention and as liquid conductors or semiconductors much in the way that liquid mercury is used in various devices. Examples of such devices include gravity switches, fluid level detecting devices and other electrical or electronic switches and sensors.

The following specific examples are present to illustrate the invention and are not to be construed as limitations thereon.

15

EXAMPLE I

1,4-Xylene bis(tetramethylene sulfonium chloride) (5g; 14.2 m mole) and 0.296 g of 2,5-dimethoxy-1,4-xylene bis(tetramethylene sulfonium chloride) (0.71 m mole) was dissolved in 37.5 ml of H₂O). The solution (0.4 M) was filtered and then degassed by N₂ for 3h. After cooling in ice bath for half an hour, a 0.4 M degassed NaOH (0.6 g NaOH in 37.4 ml H₂O) solution was syringed into the above bissulfonium salt mixture to start the polymerization. After 20 minutes, the reaction mixture was diluted by 130 ml of H₂O and neutralized by 1 M HCl to about pH7.

The resulting solution (about 200 ml) was dialyzed against deionized water from 3 to 5 days. About half of the dialyzed solution was cast into a precursor film, which was then thermally converted into the fully eliminated and conjugated conducting polymer. The elemental analysis of this conjugated polymer was: C 35 (90.22%), H(6.01%), O(3.77%). This result is consistant with 13% dimethoxy-substituted monomeric units plus 87% unsubstituted monomeric units. Intrinsic viscosity was measured to be 4.62 dl/g.

-44-

About 10 ml of the above precursor polymer solution was mixed with 3 ml aqueous solution of disodium salt of 1,3-benzene disulfonic acid (1 g, 3.5 mmole). A white fibril-like polymer precipitate was obtained. After
5 rinsing with 5 ml de-ionized water, the polymer was finger-pressed (between two glass slides) into a porous sheet-like material. The pressed polymer was then dried at room temperature overnight under dynamic vacuum.

The dried polymer was then heated (ca. 100-150°C) for
10 3 to 5 minutes under vacuum. A black-brown film (thickness about 60 microns) was obtained. The conductivity of this film was measured to be $5 \times 10^{-4} \text{ Scm}^{-1}$.

15

EXAMPLE 2

The bissulfonium salt, 2,5-dimethoxy-1,4-xylene bis(tetramethylene sulfonium chloride (1 g; 2.4 mmole), was dissolved in 6 ml of deionized water (0.4 M), and
20 degassed by N_2 for about 4h. After cooling the solution for half an hour, a 0.4 M degassed NaOH aqueous solution (0.097 g in 6 ml H_2O ; 0.4 M) was added. A cloudy polymer gel was formed within 1 to 2 minutes. The polymerization was allowed to processed for 10 minutes,
25 then 150 ml de-ionized water was added to dissolve the gel. The resulting solution was neutralized with 1 M HCl to pH 7. About 2 to 3 ml of pyridine was added to help stabilize the solution against gel formation.

The polymer solution was then placed into dialysis
30 tubes having a molecular weight cutoff of 6000-8000. These were then dialyzed against 2 to 3 liters of water containing about 5 ml pyridine. The dialysis solutions were changed every day for 3 to 5 days.

Casting the above precursor polymer solution gave a
35 transparent, light yellow-green film having a thickness of 19 microns.

This non-conductive, non-conjugated precursor polymer film was then placed at room temperature in a zip-lock bag

-45-

and sealed. After sitting at room temperature for about 2 weeks, the film was found to have become non-transparent and conductive, with a green metallic luster.

The conductivity was measured to be 10^{-2} Scm^{-1} ,
5 which is comparable to that of a fully eliminated
poly(dimethoxyphenylene vinylene) polymer film doped with
HCl.

10

15

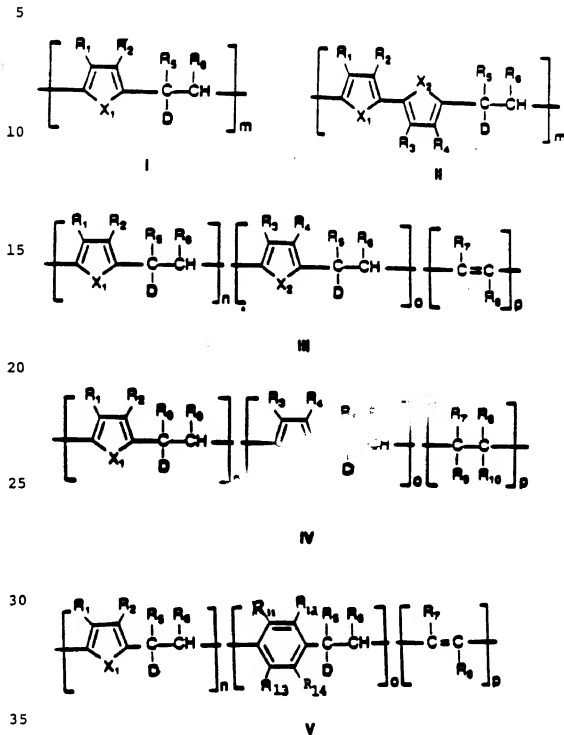
20

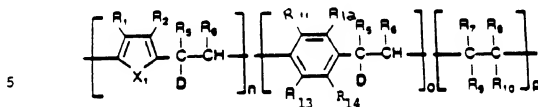
30

35

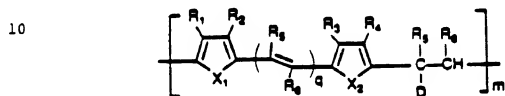
WHAT IS CLAIMED IS:

1. A homopolymer or copolymer comprising recurring units selected from the group consisting of units of the following Formulas I to XI:



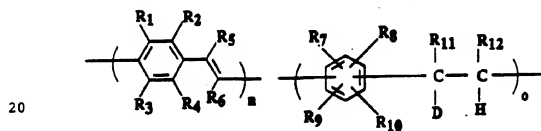


VI



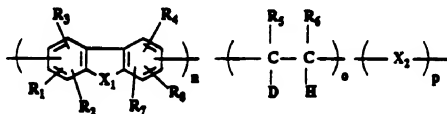
15

VII



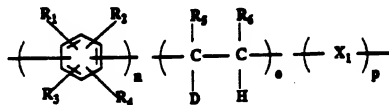
(VIII)

25

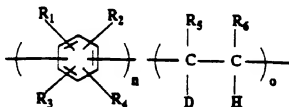


(IX)

35



(X)



(XI)

a composition comprising said homopolymer or copolymer and solutions of said composition, homopolymer, copolymer or a combination thereof wherein:

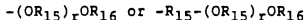
m, n, o and p are the same or different and are integers, and are selected such that m or the sum of n, o and p is greater than about 20; with the proviso that at least one of n or o is not zero;

q is an integer from 0 to about 4;

D is a leaving group with the proviso that at least about 1 mole % of D leaving groups based on the total moles of D leaving groups is a moiety which on elimination from said polymer forms a non-oxidizing protonic acid having a pKa in aqueous or non-aqueous medium equal to or less than about 4, or is a zwitterionic moiety comprising a positively charged moiety and a negatively charged moiety, at least one of which is bonded to said polymeric backbone, said anionic moiety being the conjugate base of a strong non-oxidizing protonic acid having a pKa equal to or less than about 4, which forms said acid on elimination or a moiety which on elimination forms a species which can be converted into acid;

R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, R₁₂, R₁₃ and R₁₄ are the same or different at each occurrence and are hydrogen or isotopes thereof, halogen, hydroxyl, cyano, alkyl, alkenyl, aryl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, aryloxy, alkylthioalkyl, alkynyl, alkylaryl, arylalkyl, amido, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylamino, diarylamino, alkylamino, dialkylamino, alkylarylamino,

arylthio, heteroaryl, arylsulfinyl, alkoxy carbonyl, boric acid, boric acid salts, arylsulfonyl, carboxylic acid, carboxylic acid esters, carboxylic acid anhydride, carboxylic acid salts, halogen, nitro, phosphoric acid, phosphoric acid salts, cyano, sulfonic acid, sulfonic acid salts, amino, or epoxy moieties, or a moiety of the formula:



10

wherein:

R_{15} is a divalent alkylene moiety having from 1 to about 7 carbon atoms;

R_{16} is alkyl having from 1 to about 20 carbon atoms;

15 and

r is a natural number from 1 to about 50; or any of

R_1 and R_2 , or R_3 and R_4 , or R_5 and R_6 , or R_7 and R_8 , or R_9 and R_{10} , or R_{11} and R_{12} , or R_{13} and R_{14} , or R_{15} and R_{16} , substituents taken together are an alkylene,

20

alkenylene, or alkynylene, group completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic or alicyclic carbon ring, which ring may optionally include one or more divalent heteroatoms of nitrogen, sulfur, sulfinyl, phosphorous, selenium, sulfonyl or oxygen, one or more degrees of unsaturation or a combination thereof; and

25

X_1 and X_2 are the same or different and are S, O, Se, NR_{17} , or PR_{17} , wherein R_{17} is hydrogen, R_1 , alkylaryl, arylalkyl, alkyl or aryl.

2. A homopolymer or copolymer according to claim 1

30 wherein:

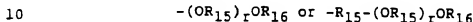
R_1 to R_4 are the same or different at each occurrence and are hydrogen; hydroxyl; alkyl containing from 1 to about 20 carbon atoms; phenyl; alkenyl containing from 2 to about 20 carbon atoms; alkylphenyl or phenylalkyl each containing from about 7 to about 20 carbon atoms;

35

alkylthio or alkoxy each containing from 1 to about 20

- 50 -

- carbon atoms; alkylamino, dialkylamino, diarylamino, arylamino and alkylarylamino; alkoxyalkyl having from 2 to about 20 carbon atoms; substituted phenyl or substituted alkyl having from 1 to about 20 carbon atoms wherein
- 5 permissible substituents are epoxy, nitro, cyano, amino, sulfonic acid and salts thereof, phosphoric acid and salts thereof, carboxylic acid and salts thereof or halo groups; moiety of the formula:

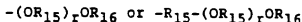


whererin:

- R_{15} is alkylene having from 1 to about 4 carbon atoms;
 R_{16} is alkyl having from 1 to about 10 carbon atoms;
- 15 and
- r is a natural number from 1 to about 25; or any of R_1 and R_2 , or R_3 and R_4 substituents taken together may form an alkylene, alkenylene or alkynylene chain having from 2 to 20 carbon atoms completing a 4, 5, 6, 7, 8, 9 or
- 20 10 membered ring system which may include one or more degrees of unsaturation and heteroatoms of divalent oxygen or sulfur.

3. A homopolymer or copolymer according to claim 2 wherein:

- 25 R_1 , R_2 , R_3 and R_4 are the same or different at each occurrence and are hydrogen, alkoxyalkyl, alkoxy, alkythio, alkyl, or moieties of the formula:



30

wherein:

- R_{15} is alkylene of about 2 to about 3 carbon atoms;
 R_{16} is alkyl of from 1 to about 3 carbon atoms; and
 r is a natural number from 1 to about 10.
- 35 4. A homopolymer of copolymer according to claim 3 wherein R_1 , R_2 , R_3 and R_4 are the same or different at

- 51 -

each occurrence and are alkyl, alkoxy or hydrogen.

5. A homopolymer or copolymer according to claim 1 wherein R_5 to R_{12} are the same or different at each occurrence and are hydrogen or alkyl having from 1 to about 12 carbon atoms.

6. A homopolymer of copolymer according to claim 1 wherein X_1 and X_2 are O, S or $-NR_{17}$ wherein R_{17} is hydrogen, alkyl of from 1 to about 12 carbon atoms or aryl from 6 to about 12 carbon atoms.

7. A homopolymer or copolymer according to claim 1 wherein D is selected from the group consisting of moieties of the formula:

$-\text{OSOR}_1$, $R_1\text{CO}_2-$, $-\text{OSO}_3R_1$, $-\text{OSiR}_1R_2R_3$, $-\text{OR}_1$,
 $-\text{OPO}(\text{OR}_1)(\text{OR}_2)$, $-\text{SR}_1R_2 \cdot Z^-$, $-\text{N}^+R_1R_2R_3 \cdot Z^-$, $-\text{P}^+R_1R_2R_3 \cdot Z^-$,
 $-\text{S}^+(\text{O})R_1R_2 \cdot Z^-$, and $-\text{N}(\text{O})R_1R_2 \cdot Z^-$;

Z is an anion of a non-oxidizing protonic acid; and

R_1 , R_2 and R_3 are the same or different at each occurrence and are hydrogen, or substituted or unsubstituted alkoxyalkyl, aryl, alkanoyl, alkoxyaryl, alkyl, aroyl, arylsulfonyl, alkanesulfonyl, alkylaryl, or arylalkyl wherein permissible substituents are one or more carboxylic acid groups, sulfonic acid groups, alkyl, alkoxy, carboxylic acid salts or sulfonic acid salts.

8. A homopolymer or copolymer according to claim 7 wherein D is a moiety of the formula $-\text{NR}_1R_2R_3 \cdot Z^-$.

9. A polymer according to claim 8 wherein $-\text{NR}_1R_2R_3$, wherein $-\text{NR}_1R_2R_3$ is pyridinium and Z^- is an anion.

10. A homopolymer or copolymer solution comprising:

(a) a solvent selected from the group consisting of water, an organic solvent and a mixture thereof; and
 (b) one or more of the homopolymers or copolymers of claim 1.

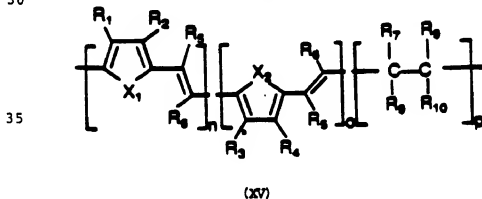
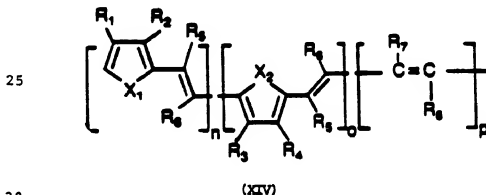
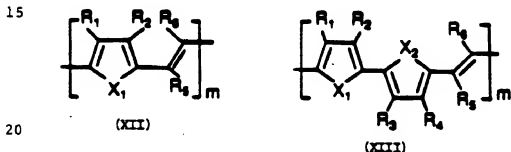
11. A method of forming an article which comprises the steps of:

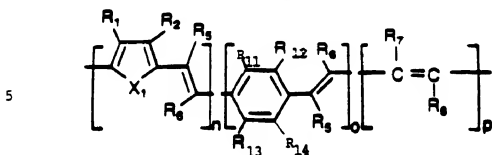
(a) forming the solution of claim 10; and
 (b) removing the solvent from the solution as the

polymer solute solidifies to form the solidified polymer having the shape of said article.

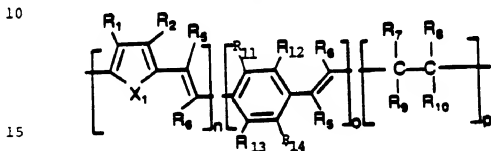
12. A method of forming a conductive article which process comprises the steps of:

- 5 (a) forming the solution of claim 10;
- (b) removing from the solution the solvent as the polymer solute solidifies;
- (c) treating said solidified polymer to eliminate the species of the formula D forming a protonic acid
- 10 species selected from the group consisting of HZ and DH
- converting said solidified polymer into a homopolymer or random or block copolymer having regular or random units of the following formulas XII to XXII:

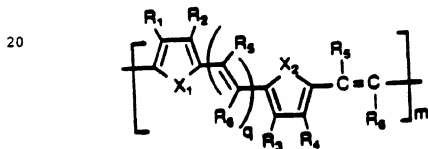




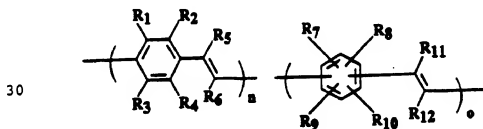
(XVI)



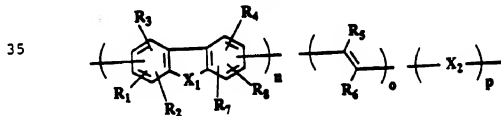
(XVII)



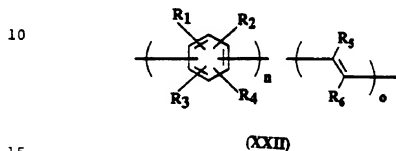
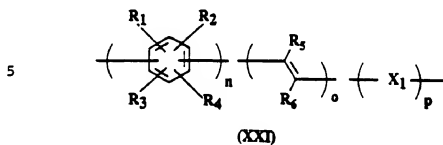
(XVIII)



(XIX)



(XX)



forming a polymer doped with said protonic acid species to a conductivity of at least about 10^{-6} S/cm.

20

25

30

35

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/02096

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 08 G 61/00, C 08 G 61/02, C 08 G 61/12, C 08 L 65/00, C 08 L 65/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ²		
Classification System	Classification Symbols	
IPC ⁵	C 08 G 61/00, C 08 L 65/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁵		
Category ⁶	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 4 900 782 (HAN et al.) 13 February 1990 (13.02.90), see claims 1-23; examples 4,5,9-12,14,15,19, 20.	1-12
X	US, A, 3 401 152 (WESSLING et al.) 10 September 1968 (10.09.68), see claims 1,8; examples I, II,VII; column 1, lines 38/ 39.	1-6, 10-12
X	J.Chem.Soc., Chem.Commun. 1987, Kwan-Yue Jen et al. "Highly-conducting Poly(2,5- Thienylene Vinylene) pre- pared via a Soluble Precursor Polymer", pages 309-311, see page 309, formulae and left column, last paragraph; page 310, left column, last para-	1-7, 10-12
<p>¹ Special categories of cited documents:¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
17 July 1991	02 Dec 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. van der Drift	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	graph and right column, first paragraph. --	
X	DE, A1, 3 704 411 (DIRECTOR-GENERAL OF AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY) 20 August 1987 (20.08.87), see claims 11,12, 1-3; column 5, lines 12-21; comparative examples 1,4; examples 1,2,4,7. --	1-7, 10-12
X	US, A. 4 808 681 (HARPER et al.) 28 February 1989 (28.02.89), see column 2, line 15 - column 5, line 12; example 1 (c), (e), (g), (h); example 5 (b), (c). --	1-7, 10-12
X	Patent Abstracts of Japan, Volume 13, No. 283 (C-612) (3631) 28 June 1989 (28.06.89), & JP-A-1 79 223 (Agency of Ind Science & Technol) 24-03-89 * Abstract * --	1-7, 10-12
X	US, A. 3 240 722 (ORTUNG et al.) 15 March 1966 (15.03.66), see claim 1; example XXVI; table "Summary" columns 17/18, A(i), (ii), (iii), column 3, line 74 - column 4, line 8. ----	1-6

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US91/02096 SAE 46553

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
in no way liable for these particulars
which are given merely for the purpose
of information.

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
dans le rapport de recherche inter-
national visé ci-dessus. Les renseigne-
ments fournis sont donnés à titre indica-
tif et n'engagent pas la responsabilité
de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US-A - 4900782	13-02-90	Keine - None - Rien	
US-A - 3401152	10-09-68	Keine - None - Rien	
DE-A1- 3704411	20-08-87	JP-A2- 1009222 DE-C2- 3704411 DE-C2- 3743443 JP-A2- 1009221 JP-A2- 1009220 JP-A2-63159429 US-A - 4868284 JP-A2-63178138 JP-A2- 1009223 JP-A2- 1020234 JP-A2- 1033140	12-01-89 03-05-89 08-02-90 12-01-89 12-01-89 02-07-88 19-09-89 22-07-88 12-01-89 24-01-89 03-02-89
US-A - 4808681	28-02-89	AT-E - 49770 CA-A1- 1265295 DE-C0- 3575569 EP-A2- 182548 EP-A3- 182548 EP-B1- 182548 GB-A0- 8429111 JP-A2-61148231 US-A - 4766198	15-02-90 30-01-90 01-03-90 28-05-86 01-07-87 24-01-90 27-12-84 05-07-86 23-08-88
US-A - 3240722		Keine - None - Rien	